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Martensitic transformation in NiTi alloy covered by protective multi-layers

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Abstract

Commercial NiTi shape memory alloy was covered with multi-layers. First, titanium nitride and titanium oxide was deposited on polished surface of the NiTi alloy. Layers were deposited in one process - a glow discharge technique. Second, on the top of the TiN/TiO_2 layer the hydroxyapatite (HAp) was deposited using electrophoresis. The HAp layer was sintered at temperature from 500^0C up to 900^0C for 5 minutes. Influence of the thermal treatments, realized during processing stages, on a course of the martensitic transformation was studied using differential scanning calorymetry (DSC).

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Keywords: Martensitic transformation; NiTi; protective layer; TiO_2 TiN; hydroxyapatite

1. Introduction

Number of practical applications of the NiTi alloys in medicine and veterinary grows from year to year. It is due to the shape memory effect and biocompatibility. However, there is still need to improve their corrosion resistance as well as osseointegration for application as a long-time implant. It can be achieved by covering surface of the NiTi alloy with multi-functional layers. Titanium oxide and titanium nitride has been found as a good candidate for layers, which sufficiently protect a human body against release of nickel ions [1]. Combining of both layers significant-

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ly improves corrosion resistance [2]. It was proved, that very thin TiN/TiO_2 can follow deformation of the NiTi matrix up to 5% [3]. From the point of view of osseintegration improvement, hydroxyapatite (HAp) has been known as ceramic, which improves functional connection between bone/tissue and surface of implant. However, consolidated HAp can be stiff and ductile. Consequently, it may crack during deformation associated with the shape memory effects. Such inconveniences can be omitted by HAp sintering at temperature, which lowers shrinkage and degree of consolidation. The presented studies were focused on influence of the thermal treatment, realized during processes applied for surface modification of the NiTi alloy.

2. Experimental data

Commercial NiTi shape memory alloy (Memry GmbH), with chemical composition: 49,4at%Ti and 50.6at.%Ni was used as a matrix for multi-layers deposition. From delivered sheets of NiTi, rectangular samples were cut in dimension of 10 mm x 8mm x 0,8 mm. All samples were quenched from 850 ^oC after 20 minutes of annealing. First, samples were subjected to nitriding/oxidizing done by glow discharge method. Deposition was carried out at 300^oC for total time: 30 minutes. Processing details can be found at [4]. Then, on the top of nitrided/oxidized surface the HAp layer was deposited using electrophoresis with parameters described at [5]. Finally, they were sintered at various temperatures (500 ^oC, 600 ^oC, 700 ^oC, 800 ^oC and 900 ^oC) for 5 minutes.

Thermal expansion of HAp was measured using dilatometer DIL 402C (NETZSCH). Measurements were done in argon atmosphere at thermal range from 20 ^oC to 1200 ^oC with a heating rate of 20 ^oC /min.

Thermal behavior of the martensitic transformation was studied with use of differential scanning calorimeter (DSC) Mettler Toledo DSC-1. Transformation temperatures of the martensitic transformation were determined from the thermograms measured with a heating/cooling rate of 10deg/min at thermal range from -120^oC to 120^oC.

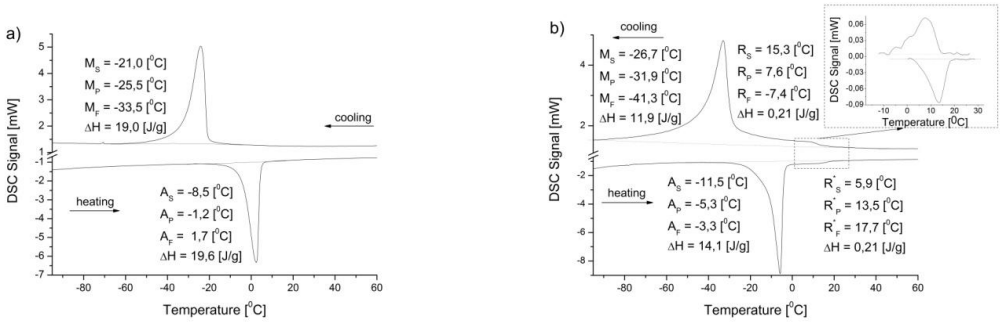

Fig. 1. DSC cooling/heating curves measured for NiTi alloy after: (a) quenching from 850 ^oC and (b) nitriding/oxidizing.

3. Results and discussion

3.1. Martensitic transformation in NiTi alloy after TiN/TiO_2 deposition

Following steps in layer deposition, first the TiN and then the TiO_2 layer was formed on surface of the NiTi alloy. An average thickness of layer was 26 nm and 32 nm for the TiN and the TiO_2 pahse, respectively [4]. Influence of the nitriding/oxidizing process on behavior of the martensitic transformation was determined from the course of the DSC cooling/heating curves (Fig.1). The as-quenched alloy reveals presence of the one-step martensitic transformation, which appears at thermal range between -33 ^oC (M_f) and 2 ^oC (A_f) (Fig. 1a). Transformation enthalpy was about 19 J/g and thermal range (M_s-M_f and A_s-A_f) - about 10 degrees during forward as well as reverse transformation. Relatively wide thermal hysteresis of the transformation suggests, that it proceeds between the B2 parent phase and the B19' monoclinic martensite. In comparison to that, thermal treatment realized during the nitriding/oxidizing process (300 ^oC/30 min.), has changed the course of the martensitic transformation. Changes concerned values of the characteristic temperatures of the martensitic transformation as well as its sequence. In general, all transforma-

tion temperatures decreased after processing. The characteristic temperatures of the forward martensitic transformation decreased of 7 degrees, whereas temperatures of the reverse transformation decreased of 4 degrees. Moreover, thermal range of the forward martensitic transformation increased up to 15 degrees, whereas for the reverse transformation it kept the same value. It means, that the reverse martensitic transformation is less sensitive to the thermal treatment done during glow discharge process. Also, applied thermal treatment took an effect on the transformation enthalpy. After processing, its value decreased from 19 J/g down to 14 J/g, which makes drop of 26%. Signal measured during DSC cooling/heating curves registration comes from the total volume of the sample. In case of studies of the covered samples, part of this volume consists of TiN/TiO_2 phases in deposited layer. Both phases are non-transformable in a sense of the martensitic transformation. Volume, which is non-transformable and comes from the thickness increase of deposited layer (57 nm), takes less than $7*10^{-5}$%. It cannot be a source of the enthalpy decrease. Structural studies done by Lelatko et. al. [3] have shown that the nitriding/oxidizing carried out at 300°C produces Ni_4Ti_3 precipitates. This phase is also non-transformable. Appearance of precipitates lowers enthalpy of the martensitic transformation and produces internal stress, which may lead to the two-steps martensitic transformation: B2↔R↔B19'.

In result of that, second influence of thermal treatment done at 300°C for 30 minutes was noticed in change of sequence of the martensitic transformation. At thermal range between -10 °C and 20 °C some deviations from the DSC base line can be observed (Fig. 1b). After mathematical correction, done for the DSC base line, additional thermal peaks were observed. One peak on cooling and one on heating DSC curves appeared (right upper corner of Figure 1b). In the NiTi alloy after glow discharge processing, enthalpy of the B2↔R transformation was 0.2 J/g. It is an evidence that this transformation occurs only in a small volume of the NiTi alloy. Taking into account the fact that formation of both phases: TiN and TiO_2 uses titanium from the NiTi matrix, its content lowers in the regions close to the surface. Simultaneously, content of nickel increases, which leads to formation of the Ni_4Ti_3 precipitations.

3.2. Transformation behavior of NiTi after hydroxyapatite sintering

Sintering of the HAp layer causes its consolidation. In consequence of that, shrinkage of the hydroxyapatite can be observed. Such phenomena produces internal stresses, which may leads to cracking of the HAp layer as well as cracking at the interface between HAp layer and the matrix. Before layer sintering for pure HAp compact the shrinkage was measured versus temperature up to 1200 °C. It has been found that up to 450 °C its value is 0%. This temperature is too low for HAp consolidation and to produce stable adhesion between HAp layer and the matrix. Sintering HAp at 500 °C caused start of its consolidation and measured shrinkage was 0,1%. For the rest applied temperatures value of the shrinkage was as follow: 0,4% (600 °C); 1,3% (700 °C); 2,2% (800 °C), 4,2% (900 °C). For HAp sintered at 1000 °C and 1200 °C shrinkage was 7,6% and 12%, respectively. This value is too high and may produce internal stresses leading to cracking and loosing adhesion during shape memory training. Taking into account obtained results covered samples were sintered in temperature from 500 °C to 900 °C.

The DSC cooling/heating curves measured for the alloy after sintering of the HAp layer, deposited on top of the TiN/TiO_2 layer, are shown in Figure 2a and 2b. Thermal treatment realized during sintering at 500 °C, took an significant effect on the course of the martensitic transformation. In comparison to the NiTi alloy, which was processed using glow discharge method, the two steps of the martensitic transformation can be clearly distinguished. The transformation between the B2 parent phase and the monoclinic martensite B19' proceeds thorough the R-phase on both cooling and heating directions. The forward transformation B2↔R is clearly separated from its second step: R↔B19'. Thermal distance between both transformation equals 26 degrees. However, the martensitic transformation proceeds in two stages – two thermal peaks (M1 and M2) appeared in region between M_{s1} (-25 °C) and M_{f2} (-52 °C) (Fig. 2c). Also, the reverse martensitic transformation occurs in two stages (A1 and A2). It can be due to well known and described mechanism:

- inhomogeneity of the chemical composition, which is caused by appearing of the Ni_4Ti_3 precipitates [6] and/or
- clasterization of the dislocations introduced during NiTi sheet production [7].

Concerning thermal position of the peaks, it can be found that distance between M1 and A1 as well as M2 and A2 equals 44 and 52 degrees, respectively. Such thermal distance is characteristic for the transformation, which leads to formation of the monoclinic martnesite B19' in reversible way. The transformation A1 overlaps on the R→B2 one. Calculation of the transformation enthalpy has shown that the transformation marked as M1 and A1 posses the same value: 7,4 J/g. Similar correlation can be found in case of M2 and A2 – the enthalpy is 4,3 J/g. Enthalpy of the B2↔R transformation is 2,2 J/g. In fully transformed NiTi alloy enthalpy for transformation B2↔B19' and B2↔R is about 20 J/g and 8 J/g, respectively. Differences in values of enthalpies can be an evidence that total volume of non-transformable phases significantly increased in NiTi alloy after HAp sintering. In general, increase of the HAp sintering temperature has changed transformation behaviour. Sintering at temperatures above 500 °C causes vanishing of the B2↔R and presence of the one-step martensitic transformation was stated. Further, no multi-stage martensitic transformation was observed. The thermal range of the forward transformation decreases from 20 degrees down to 10 degrees for sample sintered at 600 °C and 900 °C, respectively. Similarly, thermal range of the reverse transformation decrease from 12 to 9 degrees. Mainly, narrowing of the range of the forward martensitic transformation was due to increase of the M_f with increase of the HAp sintering temperature. Practically, temperatures: A_f, A_s and M_s does not depend on the value of the HAp sintering temperature and keep their value below 0 °C (Fig. 2c). The most sensitive parameter (of the martenistic transformation) to thermal treatment is transformation enthalpy. Increase of the sintering temperature causes increase its value from 14 J/g (600 °C) up to 20 J/g (800 °C). It can be due to increase of the volume of transformable phase originating in solving of the precipitates of equilibrium and non-equilibrium phases. Sintering at 900 °C did not change sequence either characteristic temperatures of the martensitic transformation., however, the enthalpy lowered to 17 J/g.

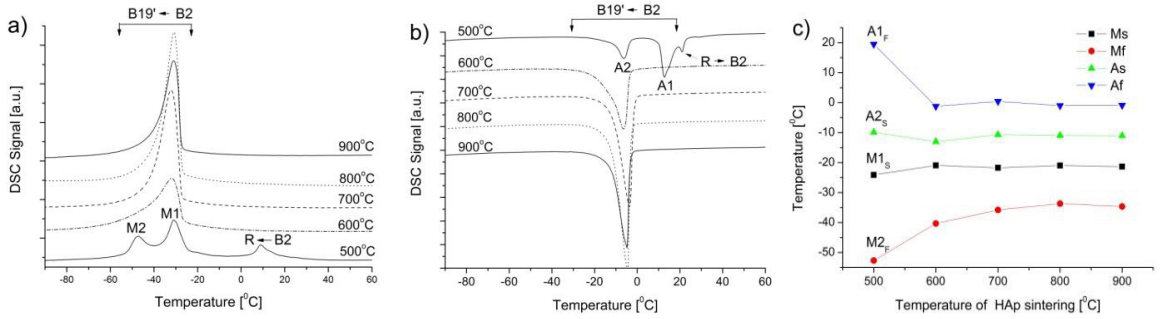

Fig. 2. Cooling (a) , heating (b) DSC curves and characteristic transformation temperatures (c) determined for NiTi alloy covered with TiN/TiO_2 and HAp after its sintering at various temperatures for 5 minutes.

4. Conclusions

Results obtained from studies can be summarized by drawing following conclusions:

- Combination of processing conditions realized during multi-layers deposition (TiN/TiO_2 and HAp layers) saves reversibility of the martensitic transformation.
- Glow discharge process (carried out at 300 °C for 30 minutes) triggers Ni_4Ti_3 precipitation process, which is enhanced by HAp sintering at 500 °C. It leads to two-steps martensitic transformation and increases its characteristic temperatures with A_f close to 20 °C.
- Sintering of the hydroxyapatite layer at temperatures between 700 °C or 800 °C causes its relatively low shrinkage, saves high transformation enthalpy and leads to lowering of the characteristic temperature down to 0 °C.
- Increase of the sintering temperature over 900 °C causes high shrinkage of the HAp as well as lowering of transformation enthalpy.

Acknowledgements

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